

D-1. University of California Scientific Peer Review

This section contains comments received from a scientific peer review conducted by four reviewers approved by the University of California Office of the President under a process defined by Health and Safety Code section 57004. The reviewers commented on the November 18, 1999 version of the main report and versions of Appendices A through D dated November 10, 1999. This version of the report is being presented at the December 9, 1999 hearing of the Air Resources Board (ARB). Each reviewer was asked to comment on the Executive Summary and sections of the report related to their particular area of expertise. The reviewers were selected by the University of California Office of the President to complement one another, so each section of the report was reviewed by at least one individual. Each comment is presented as received in normal font and is followed by the ARB staff response inserted in italics.

D-1.1. Professor Roger Atkinson of the University of California at Riverside

Attached are my comments on selected portions of the above report and its appendices

Summary

The findings of this report are supported by the evidence presented, and indicate that vehicle exhaust emissions and their impact on ozone formation will not be significantly affected by replacing one oxygenate for another, or by eliminating the oxygenate, in reformulated gasoline. In addition, the findings are consistent with previous, more restricted, investigations and/or reviews of the impacts of oxygenated (containing methyl tert-butyl ether (MTBE) or ethanol) and non-oxygenated reformulated gasolines on air quality. The report presents the results of a rather complete assessment in a logical manner, and does point out areas of uncertainty (especially in the mobile source emissions inventory).

Detailed comments are as follows:

Appendix B: Photochemical Modeling

1. Page B-6, Section B-3.1. Based on the text, I conclude that the meteorology of the August 26-28, 1987 episode was used in conjunction with the VOC and NO_x emissions appropriate for 1997 with present MTBE-containing gasoline and for 2003 with three gasolines (2.0 wt% O₂ ethanol-containing, 3.5 wt% O₂ ethanol-containing, and a non-oxygenated gasoline). This needs to be stated more explicitly than presently done. The use of "August 26-28, 1987" further on in this Appendix makes for potential confusion on the part of the reader. One specific example of this confusion is on page B-12, 13-18 lines from bottom, where the sentences state that "Figure 4.1 through 4.5 show hourly O₃, NO, and NO₂ for August 26-28, 1987, . . . The time plots clearly show that the 1997 and 2003 scenarios . . ." I suggest that it is made clear on page B-6 that all of the scenarios are for the August 26-28, 1987, meteorology and that "August 26-28, 1987" not be referred to again except on page B-32 (which deals with sensitivity studies).

Response: We have added a paragraph in Section B-3.1 explaining that the meteorology of August 26-28, 1987 will be used in all simulations, in conjunction with the appropriate VOC and NO_x emissions for the 1997 and 2003 scenarios. In addition, we have deleted

reference to August 26-28, 1987 in other parts of the report, as suggested, except on page B-32 that discusses model performance (instead of sensitivity studies as stated in the comment).

2. Pages B-8 (Table 3.3) and B-9 (Table 3.4). The "baseline boundary" and "region top" concentrations assumed for N_2O_5 (1.0 ppb) and NO_3 radicals (1.0 ppb) are unrealistically high. While the assumed NO_2 , N_2O_5 and NO_3 radical concentrations are close to equilibrium (from the $\text{NO}_2 + \text{NO}_3 \rightleftharpoons \text{N}_2\text{O}_5$ reactions), the NO_3 radical concentration is a factor of 2 higher than ever observed and a factor of 10 higher than previously observed "high" concentrations. These boundary layer and upper level concentrations need to be more realistic.

Response: A subsequent conversation with Professor Atkinson determined that 20 ppt is a more appropriate boundary and region top concentration for both N_2O_5 and NO_3 radicals. We do not expect any impact on the simulation results and overall conclusions. MTBE and ethanol do not have significant atmospheric reaction pathways with NO_3 radicals (see Section 2.1 of the main report) and the effect of lowering the NO_3 radical concentration by a factor of 50 will decrease the ozone formation potential of the alkylates, further supporting the overall conclusions of the report.

3. Page B-13, line 6. The concentrations of radical species such as OH, HO_2 , organic peroxy radicals, etc., are neither tabulated nor graphically shown in this report. I therefore suggest that "radical flux" be replaced by " O_3 , NO and NO_2 ".

Response: The suggested change has been incorporated into the report.

4. Page B-29, line 10 of text, and page B-30, line 1. Surely the emissions inventory used allows a definitive assessment of whether or not the non-motor vehicle source(s) of ethanol dominate over vehicle sources. The use of "also appears" gives the impression that no one bothered to look into it.

Response: Please note that the word "appears" is also used on page B-11, line 2 from the bottom, and on page B-12, line 2 of the text, in the same context. The emission inventory clearly shows that ethanol emissions are dominated by non-motor vehicle sources for each of the scenarios (see Appendix A, Table 4.1 through Table 4.5). To avoid any potential confusion in this matter by our choice of words, we have omitted the use of the word "appears" in the text, where appropriate.

5. Page B-29, lines 4 and 5 from bottom. I believe that "2003 3.5%" should be replaced by "2003 Et3.5%".

Response: The label has been corrected.

6. Page B-30 on. The fact that VOC emissions from vehicles using EMFAC2000 are a factor of 2-3 higher than predicted using EMPAC7G casts some doubt on the analysis carried out in the previous 30 pages of this Appendix. The use of EMFAC7G appears to be necessitated because of time-constraints, and the sensitivity analysis supports the analysis using the EMFAC7G emissions inventory in that replacing MTBE in gasoline by ethanol (or removing the oxygenates altogether) will have no significant impact on air quality. However, the uncertainties in the mobile source emissions inventory (or the use of an

outdated emissions inventory) is troubling and leads to uncertainties in the 2003 (and 1997!) predicted air quality contained in this report. A number of questions arise:

Is the 1987 inventory (and hence the comparison of predicted vs observed 1987 ambient concentrations) subject to changes in the mobile source VOC and NO_x emissions ?

Is the 1997 inventory, multiplied by the factor of 3, realistic - and if so then the LA Basin maximum O₃ levels could have been (if the meteorology had been conducive to it) almost as high as 1970's values (400 ppb). Since 1997 has come and gone (with a large-scale field study for ozone having been conducted), what does modeling the 1997-SCOS data tell us about the mobile source inventory ?

If the 2003 inventories used in Tables 5.1 and 5.2 are close to reality then O₃ levels in the basin may well increase significantly over the next few years.

Why weren't the NO_x emissions increased as indicated by EMFAC2000, and what is the impact of increasing vehicle NO_x emissions by a factor of 1.8 ?

This rather casual mention of (in essence) "and by the way the real VOC and NO_x emissions from vehicles are believed to be higher than used by factors of around 2.3 and 1.8, respectively" subtracts from the credibility of this report. Significantly more discussion needs to be given concerning the "real" 1987, 1997 and 2003 inventories (or at least CARB's best opinion of them) and the implications for maximum (and 8-hr) O₃ levels. As mentioned above, surely the 2003 inventories should use VOCs increased by a factor of 2.3 and NO_x by a factor of 1.8 in addition to, or instead of, those used in Table 5.1.

Response: The new California on-road motor vehicle emission factor model, EMFAC2000, is still under development and we are reluctant to use it until it receives public scrutiny and possible Board approval in March 2000. We are conducting a detailed in-house comparison of EMFAC2000 against "top-down" studies (i.e., tunnel, ambient ratio, fuel-based). The Singer and Harley (1999) fuel-based inventory discussed in the report is for stabilized exhaust emissions and does not include cold start or evaporative emissions, so it is not necessarily inconsistent with EMFAC2000. We also have some concerns with Singer and Harley's methodology (primarily lack of freeway measurements where gm/gallon emission rates are likely to be lower) and view it as an upper-bound estimate. We share your concern that EMFAC2000 will increase the 1987 inventory and significantly erode model performance, and may predict 1997 ozone levels well above those observed in July 1998 (0.244 ppm maximum) when meteorology was more conducive to high ozone than in August 1987. Unfortunately, SCOS97-NARSTO modeling results will not be available until sometime late next year. Because of these concerns, we tripled the gasoline-related VOC emissions to bracket the effect of EMFAC2000. Increasing the VOC emissions without concurrent increase in NO_x maximizes the effect on photochemically generated pollutants and is consistent with producing an upper-bound. More complete results and discussion are included in the revised report.

7. Page B-31, first paragraph of text. Reaction with O₃ will not be the dominant loss process for 1,3-butadiene during daylight hours. Even assuming 200 ppb of O₃ and 1.0×10^6 molecule cm⁻³ of OH (a low daytime value), the OH radical reaction is a factor of 2 faster than the O₃ reaction.

Response: We agree with the comment that during daylight hours the OH radical reaction is the dominant loss process, with the OH radical reaction a factor of 2 faster than the O₃ reaction (when using the O₃ and OH radical concentrations in the comment). However, we did not mention in the report that the model predicted that the peak 1,3-butadiene was at 0400 hours, where nighttime reactions with O₃ and NO₃ radicals are the important loss processes. Assuming a nighttime O₃ concentration of 100 ppb, and a NO₃ radical concentration of 0.02 ppb, the NO₃ radical reaction is a factor of 3 faster than the O₃ reaction. The lack of sensitivity of the 1,3-butadiene domain peak to emission changes in the sensitivity scenarios was incorrectly attributed to an increase in its reaction with ozone. The domain peak 1,3-butadiene also happens at the same location in Ventura County for all sensitivity scenarios because a local source is influencing the domain peak. Our text in page B-31 was modified to reflect this finding.

8. Page B-40, line 4. Replace "under predict PAN" by "underpredicts PAN".

Response: The text has been corrected.

9. Page B-43, line 1. Replace "compared" by "compare".

Response: The text has been corrected.

10. Page B-46, Table 7-1. The rate parameters given in this table for PAN formation and decomposition use the Troe fall-off expression. Somewhere (here or in Attachment B.1) the Troe fall-off expression needs to be given and the parameters used therein defined. Otherwise Table 7.1 is useless.

Response: We have included expressions for the rate constant parameters used in the SAPRC97 mechanism at the bottom of Table 7-1, and also at the beginning of Attachment B1.

11. Page B-49. For essentially all of the individual compounds shown in Figures, the O₃ formation potentials vary significantly. Some discussion of why this variation occurs (different VOC/NO_x ratio, etc. ?) needs to be given. The O₃ formation potentials should be compared on a relative basis to see if the variations of the absolute numbers diminish. In my opinion, this complete section (B-7) dealing with O₃, PAN and PPN formation potentials could be deleted with no adverse impact on the report.

Response: Ozone formation potentials are dependent on local ambient conditions, such as the VOC/NO_x ratio and the chemical composition (Carter and Atkinson, 1989; Derwent and Jenkin, 1991). Additional variability is introduced from the lack of complete VOC speciation for some of the historical episodes and differences in lumped reaction rates. This explanation is now contained in the text. We believe the box modeling complements the airshed model's finding that ethanol and directly emitted acetaldehyde are not major contributors to ozone and PAN formation and is a necessary part of the analysis.

12. Page B-49, PPN formation potentials. A minor point: because PPN is a "lumped" higher peroxyacyl nitrate, the data cannot indicate which specific higher PAN is involved.

Response: Elsewhere in the report we have noted that PPN represents peroxypropionyl nitrate and higher molecular weight acyl peroxy nitrates. We have modified the text to reflect the lumped nature of PPN.

13. Page B-56, Table 7.5. The heading for this table caused me some confusion (because of the words "total" and "individual"), and may be better given as "Contribution from individual VOCs to ozone formation", since $(\text{OFP})_i(\text{VOC})_i$ is the amount of ozone predicted to be formed because of the presence of VOC_i .

Response: Similar headings are used in Table 7.6 through Table 7.10 and can also be a potential source of confusion for the reader. We have used the suggested text in the headings for Table 7.5 through Table 7.10.

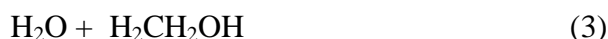
14. Page B-61, last sentence. I am surprised that acetaldehyde does not have a significant contribution to PAN formation, because PAN formation arises from the OH radical-initiated reaction of acetaldehyde and from the production of acetyl radicals arising from alkoxy radical decomposition reactions. I suspect that this "acetaldehyde" is that directly-emitted (or initially present) and does not include acetaldehyde formed *in situ* in the atmosphere from VOCs (including from ethanol) [this would then be consistent with the data in Table 7.11]. If so, this needs to be stated.

Response: You correctly inferred that the ozone, PAN, and PPN (including higher molecular weights acyl peroxy nitrates) formation potentials of a given VOC were estimated from the initial VOC concentration. This is the same methodology used by Bowman and Seinfeld (1994). This was made clear only for the ozone formation potential on page B-44, where it says "the ozone forming potential can be estimated as the local sensitivity of the predicted ozone concentration to the initial concentrations of each organic compound in the mixture". We have added this clarification in Section B-7 where appropriate.

15. Attachment B1, page B-66. See Comment #10. Also a legend for the kinetic parameters should be given at the beginning of this section. After looking at the OH + ethanol and OH + MTBE rate constants, I figured out that the parameters are A ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), E (kcal mol^{-1}) and n in $k = A(T/300)^n e^{-E/RT}$.

Response: We have added a description of the kinetic parameters used in the SAPRC97 chemical mechanism at the beginning of Appendix B1.

16. Attachment B3, page B-74, and also Executive Summary, section 2.1.2. The most recent (1997 and 1999) IUPAC evaluations and that of Atkinson (*J. Phys. Chem. Ref. Data*, **Monograph 2**, 1-216, 1994) recommend that the OH + ethanol reaction proceeds by (reaction channels numbered as in the Executive Summary):



with channels (3) and (5) each accounting for 5^{+10}_{-5} % of the overall reaction at 298 K. The relative importance of reaction (5) in the IUPAC evaluations and in Atkinson (1994) is based on the assumption that H-atom abstraction from the O-H group in ethanol occurs with a rate constant equal to that for the corresponding reaction in methanol. The rate constant for reaction (3) is based on an estimation and on the elevated temperature data of Hess and Tully (see the above references). In the atmosphere, reactions (4) and (5) give rise to the same products (acetaldehyde plus HO_2) and are hence indistinguishable.

Response: The suggestion will have a slight impact on the product yield parameters currently used in the SAPRC97 chemical mechanism currently implemented in the UAM-FCM. We defer to Dr. Carter to provide us with a representation of the OH + ethanol reaction appropriate for the airshed model simulation and will use the updated reaction in any future simulations. In addition, based on a follow-up discussion with Professor Atkinson, we will also use an updated OH + ethanol reaction rate constant according to the most recent IUPAC recommendation of $k=5.56 \times 10^{-13} (T/300)^2 \exp(532/T)$ (Atkinson et al, 1999).

17. Attachment B3, page B-74, and also Executive Summary. The OH + MTBE mechanism is "lumped" in that the specific products are not represented as such. However, this is not going to make any difference for ozone predictions. The rate parameters used for OH + MTBE are from Atkinson (*J. Phys. Chem. Ref. Data*, **Monograph 1**, 1-246, 1989) and have been superseded by a very slightly different rate constant in Atkinson (1994).

Response: The OH + MTBE reaction in the SAPRC97 chemical mechanism uses a lumped representation of the reaction products, which is deemed appropriate for airshed model simulations. A detailed mechanism with inclusion of all the potential reaction channels is not possible, since it will be very computer resource intensive. Hence, to save time, and at the same time have a good representation of the overall effect of a reaction (including the reactions of the products), a lumped representation is appropriate. Please note that the same approach is used for the other "explicit" mechanisms used in the model. These representations of explicit mechanisms are available by Dr. W.P.L. Carter at his web page ([ftp://cert.ucr.edu/pub/carter/mech/saprc97](http://cert.ucr.edu/pub/carter/mech/saprc97)). The OH + MTBE reaction rate constant will be slightly modified to according to the comment in any future air quality simulations.

Staff Report

18. Page 2, Executive Summary. Two typographical errors.

On line 20, sentence starting "Prior studies". "greater" should be "greater than".

10 lines from bottom, "decreases" should be "decrease".

Response: The text has been corrected.

19. Page 3, Executive Summary. The discussion concerning the increased VOC emissions predicted using EMFAC2000 glosses over the fact that (at least with the emissions scenarios used in the sensitivity studies and using the August 26-28, 1987 meteorology) the predicted maximum ozone levels are 300 ppb for 2003 and the peak 1-hr PAN concentrations are increased by a factor of 3. As noted above in Comment #6, the use of the "correct" emissions (or the most up-to-date estimates) for both VOCs and NO_x would have been optimum. For the scenarios given in Table 1, the basin may be NO_x-limited and relatively small changes in VOC emissions and/or profiles would then have little or no effect on ozone.

Response: See response to Comment #6 above.

20. Page 6, Section 2.1.1. The rate constant cited is from Atkinson (1994) [IUPAC (Atkinson et al. 1999a) did not evaluate OH + MTBE]; see also Comment #17 above. The product data cited are correct; however, it should be noted that these data are for NO being present and are therefore applicable to urban areas but possibly not to downwind areas with low NO_x

concentrations. Based on the same studies used by Koshland *et al.* (1998), the reaction mechanism in the presence of NO has been discussed in more detail by Atkinson (1994) and a product profile of *tert*-butyl formate (76%), formaldehyde (48%), methyl acetate (18%) and acetone (6%) recommended [formation of *tert*-butyl nitrite was observed in one of the laboratory studies due to the $(\text{CH}_3)_3\text{C} + \text{NO} \rightarrow (\text{CH}_3)_3\text{CONO}$ reaction competing with the $(\text{CH}_3)_3\text{C} \rightarrow \text{CH}_3\text{C}(\text{O})\text{CH}_3 + \text{H}_3$ decomposition reaction; under atmospheric conditions the decomposition reaction will totally dominate]. No comment is made concerning the products expected to be formed at low NO_x concentrations from the reactions of $(\text{CH}_3)_3\text{COCH}_2\text{O}$ and $\text{CH}_3\text{OC}(\text{CH}_3)_2\text{CH}_2\text{O}$ radicals with HO_2 and R_2 radicals, namely $(\text{CH}_3)_3\text{COCH}_2\text{OOH}$, $(\text{CH}_3)_3\text{COCHO}$ (also formed in the presence of NO as noted above and in the Executive Summary), $(\text{CH}_3)_3\text{COCH}_2\text{OH}$, $\text{CH}_3\text{OC}(\text{CH}_3)_2\text{CH}_2\text{OOH}$, $\text{CH}_3\text{OC}(\text{CH}_3)_2\text{CH}_2\text{OH}$ and $\text{CH}_3\text{OC}(\text{CH}_3)_2\text{CHO}$ (plus HCHO, methyl acetate and acetone formed from the $\text{CH}_3\text{OC}(\text{CH}_3)_2\text{CH}_2$ and $(\text{CH}_3)_3\text{COCH}_2$ radicals). Some mention should be made that *tert*-butyl formate is less reactive in the atmosphere than is MTBE (by about a factor of 4).

Response: The suggested changes have been incorporated into the report.

21. Page 6, Section 2.1.2. See Comment #16 above. Reaction pathway (5) has not been shown experimentally to be negligible under atmospheric conditions, and the only experimental data concerning the importance of the three possible reaction channels are a branching ratio of $k_4/(k_3 + k_4 + k_5) = 0.75 \pm 0.15$ at room temperature (Meier *et al.*, *Chem. Phys. Lett.*, **115**, 221-225, 1985; *Ber. Bunsenges. Phys. Chem.*, **89**, 325-327, 1985) and an acetaldehyde yield under atmospheric conditions of $80 \pm 15\%$ (Carter *et al.*, *J. Phys. Chem.*, **83**, 2305-2311, 1979). The formation of CH_3HOH and CH_3CH_2 radicals from reactions (4) and (5) lead to the formation of acetaldehyde plus HO_2 , independent of the presence or absence of NO, and hence the data of Carter *et al.* (1979) indicate that $(k_4 + k_5)/(k_3 + k_4 + k_5) = 0.80 \pm 0.15$. Formation of HOCH_2H_2 radicals leads to the formation of glycolaldehyde [HOCH_2CHO] (22%) and $\text{HCHO} + \text{HCHO}$ (78%) in the presence of NO (yields are for 298 K and atmospheric pressure of air), and to $\text{HOCH}_2\text{CH}_2\text{OOH}$, $\text{HOCH}_2\text{CH}_2\text{OH}$, HOCH_2CHO and HCHO in the absence of NO. The atmospheric reactions of the HOCH_2H_2 radical have been reviewed by Atkinson (*J. Phys. Chem. Ref. Data*, **26**, 215-290, 1997). Formation of methyl nitrate is not expected to be of any significance; rather the formation of ethyl nitrate in very small overall yield ($<0.1\%$) could occur from the reaction of the ethyl peroxy radical with NO.

Response: The suggested changes have been incorporated into the report.

22. Page 7, Section 2.1.3. The atmospheric chemistry of the "alkylates" was most recently reviewed and evaluated by Atkinson (1997). The rate constants for $\text{NO}_3 + \text{C}_4$ alkanes at 298 K range from $5 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ to $4 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 1997); the rate constants ascribed to Aschmann and Atkinson (1995) are incorrect by 4 orders of magnitude. The products observed and expected in the presence of NO include carbonyls, alkyl nitrates, hydroxycarbonyls and hydroxynitrates, and at low NO_x concentrations will include hydroperoxides, alcohols, hydroxycarbonyls, diols, and hydroxyhydroperoxides (Atkinson, 1997).

Response: The suggested changes have been incorporated into the report.

23. Page 8, Table 2.1. The use of a 12-hr daytime OH radical concentration of 1.6×10^6 molecule cm^{-3} seems low, because the global tropospheric 24-hr (annual) average OH radical concentration is 1.0×10^6 molecule cm^{-3} (Prinn *et al.*, *Science*, **269**, 197-192, 1995).

Response: Table 2.1 has been updated with a 12-hour daytime OH radical concentration of 3×10^6 molecule cm^{-3} , as suggested by Professor Atkinson in a subsequent conversation.

24. Page 8, Section 2.1.5. Should include the formation of hydroxycarbonyls and hydroxynitrates from alkylates.

Response: The suggested change has been incorporated into the report.

25. Page 16, footnote 5. I suspect that on line 7 of this footnote, the "RVP of about 8.5" should be "RVP of about 7.5" [further on it is stated that there will be a 1.0 psi increase (from the 6.5 psi of the gasoline mixture)].

Response: The text has been corrected.

Appendix B: Emissions

26. Page A-17, 9 lines from bottom. Why was the SAPRC97 mechanism not used for these reactivity calculations ? The NRC (1999) report shows that the absolute MIRs change significantly from SAPRC90 to SAPRC97, although on a relative basis the changes are much less. On line 12 from bottom, the units of specific reactivity ($\text{gO}_3/\text{g organic}$) should be given.

Response: A complete set of SAPRC97 MIR values were not available for these comparisons. While the SAPRC90 values do not necessarily represent the SAPRC97 mechanism, the inclusion of average reactivity is only for comparison purposes. The results of the photochemical modeling are unaffected by the MIR scale used.

27. Page A-19. Units need to be given for the data in Tables 3.7 and 3.8.

Response: Table 3.7 now clarifies that the units are gram ozone/gram NMOG. Table 3.8 is a listing of profile codes used for the alternate scenarios so there are no units.

28. Page A-24 states that vegetative emissions were incorporated into the source inventory, yet Table 4.1, under "natural sources", has only "wildfires". Some comment is needed.

Response: The text on this page now states that the total vegetative emissions from the SCAQS August episode are 103.5, 128.8, and 139.8 tons/day for August 26, 27, and 28, respectively. Since these vegetative emissions are constant for all scenarios they do not affect the anthropogenic emission comparisons.

29. Page A-47. The units at the head of this table (kilogram moles/day) appear incorrect; either kilograms/day or moles/day.

Response: The correct units of kilomoles/day are now noted on Table 4.9.

D-1.2. Professor Barbara J. Finlayson-Pitts of the University of California

As per your request, I have reviewed the Staff Report, "Air Quality Impacts of the Use of Ethanol in California Reformulated Gasoline", and my comments are attached. Overall, the ARB

staff have done a good job in this initial examination of the potential effects of the use of ethanol in fuels, especially given the time constraints.

As you can see from the first part of my comments, my major concern is that historically, emissions from vehicles have been underestimated both in California and nationally. As a result, what might have been thought in the past to be unrealistic “worst case” scenarios have turned out to be closer to reality. Because of this, I think that it would be important for the ARB to treat some “worst case” scenarios for ethanol use (e.g. in which the RVP is assumed to be higher than 7, the canisters are assumed to malfunction etc.).

I think this is particularly important in that despite all the caveats in the report, this initial assessment will likely end up being used extensively both inside and outside California. I fear that the preliminary assessment may give a misleadingly positive impression which may not ultimately be representative of the “real world” effects.

Response: We now more fully discuss the results of the ARB (1998) analysis of a non-complying ethanol-blended fuel (which shows significant air quality impacts) in the main report and Executive Summary. This serves both as a caution that it is important to meet the RVP requirements (including addressing the commingling and permeation issues) and to not extend our findings to the parts of the country (non-Federal RFG areas) that the U.S. EPA allows an RVP exemption for ethanol.

COMMENTS ON DRAFT REPORT:

AIR QUALITY IMPACTS OF THE USE OF ETHANOL IN CALIFORNIA REFORMULATED GASOLINE

This report is a good initial approach to addressing air quality impacts from the potential future use of ethanol in reformulated gasoline. Appropriately, it includes a number of caveats and areas of uncertainty which will be the subject of ongoing work by the ARB on this problem.

My major concern is that this report will be taken by many, both inside and outside California, as a final assessment. As such, the initial conclusions regarding potential impacts on air quality being minimal are likely to be cited in a widespread manner. However, as detailed in the following comments, I believe that this may change significantly as new data become available, and hence the initial impression left by this assessment may be overly optimistic. In this regard, I have two major concerns, one regarding the emissions estimates and one regarding the use of population-weighted exposures.

Major Overall Concerns:

Emissions: The history of air pollution both in California and the U.S. shows that emissions, particularly from motor vehicles, have been significantly underestimated. This was pointed out, for example, in the 1991 National Research Council Report *Rethinking the Ozone Problem in Urban and Regional Air Pollution*. Adjustments were subsequently made to motor vehicle emission models, but as this current draft report on ethanol points out, the EMFAC2000 model is expected to include additional new multiplication factors of 2.3 for VOC and 1.8 for NO_x. These very large adjustments were not foreseen by the scientific community, and it is not clear to me that the reasons for the underestimations are thoroughly understood even today.

Response: We agree and that is why our study included a review of ambient air quality studies for areas that have already introduced large amounts of ethanol into their fuel supply and why we have already implemented an ambient air quality measurement program to provide a “real-world” check on our analysis. This is now discussed more thoroughly in the main report and Executive Summary.

This history suggests to me that what are often taken as “worst cases” end up being more typical cases. In the particular case of ethanol, there are some areas of uncertainty discussed in the report which are already known to possibly contribute to underestimates of emissions:

1. The Executive Summary states that “Our analysis did not include the possibility of increased evaporative emissions due to reduced canister function or commingling”. The issue of impacts on canister function is discussed in detail on page 15, where it is pointed out that “Oxygenates such as ethanol and MTBE bind more tightly to the activated carbon than hydrocarbons such as butane..... may have the effect of reducing the canister’s working capacity. Additionally, ethanol is hygroscopic (i.e. attracts water) and water is clearly known to reduce working capacity...”.

Response: These issues are prominent in the California Phase 3 Reformulated Gasoline Regulations and the report now includes additional discussion on steps being taken to address these issues.

2. Throughout the report, it appears to be assumed that the RVP will not increase with the use of ethanol because of the California RVP requirements. In the Executive Summary, it is stated that the “impact on acetaldehyde concentrations is substantial only in Brazil, where the fuels contain either neat ethanol or 22 vol% ethanol. Due to the lack of RVP requirements for gasolines in Brazil, this acetaldehyde increase could be due to the addition of substantial evaporative emission, rather than strictly the results of an ethanol-for-MTBE substitution”.

The summary of recent assessments in Section 2.2 cites many studies where ethanol has been stated to significantly increase species such as acetaldehyde and PAN, but these are dismissed as not being germane. For example, in Section 2.2.1 in the discussion of the University of California MTBE report, it is stated: “However, these findings are not applicable to fully complying CaRFG2 fuels that have the same Reid vapor pressure (RVP) requirement and are constrained by the ARB Predictive Model .. to meet the same limits on exhaust emissions of VOC, NO_x and cancer risk-weighted toxic air contaminants.” On page 19, with regard to the predicted emissions, it is stated that “For the three fully complying non-MTBE gasolines, the ARB Predictive Model (ARB, 1995) constrains the total mass emissions of VOC and NO_x, so emissions of these pollutants were held constant for all the 2003 scenarios”.

These assumptions may indeed be the case but it seems to me that given the history of underpredicting emissions, the possibility of increased emissions in the “real-world” should not be discounted. This may be particularly important since as pointed out on page 15, “Hot soak emissions from a test program conducted by the ARB (1998b) using a blend of 10 vol% ethanol with an RVP of 7.8 psi confirmed that the proportion of ethanol in the vapor was higher than in the fuel. In this case, the proportion of ethanol in the vapor was on the order of 25 to 50 wt%..”.

Response: We now more fully discuss the results of the ARB (1998) analysis of a non-complying ethanol-blended fuel (which shows significant air quality impacts) in the main report. This serves both as a caution that it is important to meet the RVP requirements (including addressing the commingling and permeation issues) and to not extend our findings to the parts of the country (non-Federal RFG areas) that the U.S. EPA allows an RVP exemption for ethanol.

3. On page 5, it states that “We also did not consider the possible mileage penalty from increasing the oxygen content of the ethanol-containing gasoline to 3.5 wt %”. I do not know what sort of penalty this would be or the effects on emissions, but again, this is an example of a potential source of underestimation.

Response: Relative to typical current CaRFG2 made with MTBE, CaRFG2 containing 2 wt% oxygen as ethanol would only provide a slightly different fuel economy (change of 0.6% or less). CaRFG2 with 3.5 wt% oxygen would likely provide less fuel economy (by ~2%) than current gasoline, while a non-oxygenated CaRFG2 would improve fuel economy by ~2%. However, mass emissions rate should not change in proportion to the change in fuel economy. The Predictive Model tends to force emissions to meet constant standards regardless of the oxygen content. The model is built from data on emissions versus oxygen content of gasoline, with emissions measured in mass per mile, not in mass per volume of fuel.

4. It is not clear to me whether evaporative emissions during refueling were considered in the air quality analysis?

Response: All sources with either gasoline evaporative or gasoline exhaust emissions reflect gasoline reformulation. Evaporative losses from refueling or storage evaporation were assigned the headspace vapor organic gas species profile. All exhaust from off-road gasoline engines were assigned the non-catalyst stabilized organic species profile.

The report does point out that many of these issues are being examined, but again, my fear is that this *initial* assessment, which indicates there will be little impact on air quality due to the use of ethanol, will tend to be the one which will be generally used.

I would recommend that some “worst case” scenario’s be treated in which it is assumed that the mandated requirements are not met, e.g. the RVP is higher than 7.0, the evaporative emissions are greater and have relatively more ethanol etc. These could provide some idea of what could happen in an less-than-ideal control scenario.

Response: See response to Comment #4 above.

Use of Population-Weighted Exposures: The results of the photochemical modeling are summarized in Tables 4.4 – 4.6 for four scenarios. While Table 4.6 shows population-weighted exposure, maximum daily average and maximum 1-hour average for a variety of pollutants, Tables 4.4 and 3.5 show only the population-weighted averages for the organics of major concern, acetaldehyde, ethanol and formaldehyde. Air quality standards both in California and the U.S. are expressed in terms of maxima for a given time span, not as population-weighted values. There are clearly many potential problems with the use of population-weighted values. While it appears that the ARB was asked by OEHA to express the modeling results in part in this form (page 26), I am particularly concerned to see only the population weighted data cited in Tables 4.4 and 4.5. The same is true of the air quality numbers in Tables 4.8 and 4.9. I recommend that the 1-hour, and

where appropriate the 8-hour, maxima be cited first and the emphasis put on these values since they represent estimates of the effects expected on the ambient concentrations due to the introduction of ethanol.

Response: The staff agrees that the averaging times presented in Table 4.4 and Table 4.5 are not as comprehensive as the information presented in Table 4.6 and this has been corrected in the final report. The purpose of Table 4.8 and Table 4.9 is to present a reality check between the changes in estimated emissions and modeled air quality. Since the emissions estimates represent a typical summer day it is more appropriate to compare these results with the 24-hour population-weighted modeled air quality results.

Comments and Questions on Modeling:

1. There is an increasing recognition [e.g. De Haan *et al.* *Int. Rev. Phys. Chem.* **18**, 343 (1999)] that chlorine atoms may play a role in the oxidation of organics in coastal areas, which includes such major California cities as Los Angeles, San Francisco and San Diego. Specific measurements of Cl_2 [Spicer *et al.*, *Nature* **394**, 353 (1998)] and non-specific measurements of photolyzable chlorine compounds in coastal areas in the eastern U.S. [e.g. Keene *et al.*, *Environ. Sci. Technol.*, **27**, 866 (1993)] find nighttime concentrations of Cl_2 (and perhaps other species) of ~ 150 ppt. At dawn, photolysis generates highly reactive chlorine atoms at concentrations up to $\sim 1 \times 10^5$ atoms cm^{-3} . There is also evidence for a continuous daytime source of Cl atoms, giving a steady-state Cl atom concentration of as much as mid- 10^4 Cl atoms cm^{-3} at noon over the somewhat polluted North Atlantic Ocean [Wingenter *et al.*, **101**, 4331 (1996)]. The rate constants for oxidation of ethanol and MTBE by OH are similar ($\sim 3 \times 10^{-12}$ cm^3 molecules $^{-1}$ s $^{-1}$), giving estimated atmospheric lifetimes of 53-59 hours for OH at 1.6×10^6 cm^{-3} , or 530-590 hours at 1.6×10^5 cm^{-3} which might be typical of early morning hours. The Cl + ethanol rate constant is 9.4×10^{-11} cm^3 molecules $^{-1}$ s $^{-1}$ and that for Cl + MTBE is 1.66×10^{-10} cm^3 molecules $^{-1}$ s $^{-1}$, corresponding to lifetimes of about 30 and 17 hours respectively at a Cl atom concentration of 1×10^5 cm^{-3} which appears to be reasonable for the early morning hours. That is, if indeed chlorine atom chemistry is important in coastal regions, the oxidations of these oxygenates may be speeded up significantly. It might therefore be worthwhile considering doing some modeling runs with a concentration of Cl_2 of about 10^5 cm^{-3} at dawn (each day, not just the first day which is not used in the modeling results) and a steady-state daytime concentration at the coast of $\sim 10^4$ cm^{-3} to see the effect, if any, on the formation of formaldehyde, acetaldehyde and PAN.

Response: There is a chlorine chemistry module available in the SAPRC97 mechanism and, hence, it could be added to our atmospheric chemical mechanism (W.P.L. Carter, personal communication, 1999). However, chlorine chemistry was not included in our simulations, since we were unaware of the potential significance of the chlorine radical reaction with hydrocarbons, such as ethanol and MTBE. Note that chlorine chemistry is also not included in the more recent SAPRC99 (Carter, 1999). There are significant uncertainties in the reliability of models on chlorine chemistry because there are limited smog chamber data to test mechanisms for chlorine radical reactions (Carter, personal communication, 1999). We are currently conducting a simulation to bound the effect of chlorine chemistry by adding the Cl + ethanol rate constant suggested above and an

upper-bound chlorine atom concentration of 10^5 Cl atoms cm^{-3} throughout the entire modeling domain for all hours, not just coastal areas during daylight hours. We will add the relevant chlorine radical reactions to any future air quality modeling.

2. Some of the model predictions do not seem to make sense intuitively. For example, Table 4.4 shows that the 1-hour PAN maximum will be lower for the 2003 Et2.0% scenario compared to the 2003 MTBE scenario. Similarly, Table 4.6 shows that although the maximum 1-hour average and maximum daily average ethanol concentrations are expected to be about 50% greater for the 2003 Et2.0% scenario compared to the 2003 MTBE scenario, acetaldehyde and PAN concentrations are predicted either not to be affected at all, or in the case of the 1-hour maximum PAN levels, even decrease. There should be some discussion of the reasons for these surprising results.

Response: The difference in predicted PAN concentrations is due to the differences in the emissions inventories for each scenario. From Table 4.9 in page A-45, it is clear that the 2003 Et2.0% has a higher ethanol content than the 2003 MTBE. However, the 2003 MTBE has a higher content of aromatics, alkanes, and olefins, compared to the 2003 Et2.0%. Figures 7.3 and 7.4, in pages B-51 and B-52, respectively, suggest that the lumped species ALK1, ALK2, ARO2, OLE1, and OLE2 can have (depending on the environmental conditions) a higher PAN forming potential, compared to that from ethanol. Another factor is that although ethanol emissions are higher in the 2003 Et2.0% scenario, they only represent 8 percent of the non-methane VOC emissions. For comparison, ALK1, ALK2, ARO1, OLE1 and OLE2 comprise about 60 percent of the non-methane VOC emissions. Hence, PAN formation is mainly determined by the differences in alkane, aromatic, and olefinic content between scenarios. This discussion has been included in the report.

3. The concentration of CO_2 in Tables 3.3, 3.4 and 3.5 should be 358 ppm, not 1 ppm (no difference to chemistry, I assume, since condensed phase chemistry where CO_2 would act as a buffer is not included). The boundary, top and initial species HONO concentrations also seem low for the Los Angeles region, where something of the order of 1 ppb might be more applicable [e.g. Winer and Biermann, *Res. Chem. Inter.* **20**, 423 (1994)]. In Table 7.4, the methane concentration must be about 1.7 ppm, since this is a global average; smaller values as shown in the table don't seem reasonable.

Response: CO_2 concentrations do not have an effect on the photochemistry and the major source of HONO is direct emissions (assumed to be 2% of the NO_x) and in situ formation. In any future modeling we will revise the boundary, top, and initial conditions that we use for CO_2 and HONO. The methane concentration used in the Brazilian box model simulations is a mistake that has now been corrected.

4. In Appendix B on pages B-11 and B-12, it is stated that "Although domain ethanol emissions have increased from 1997 to 2003, reflecting changes to the motor vehicle cleaner burning gasoline used, the emissions from non-motor vehicle sources (which appear to dominate the magnitude of the maximum ethanol concentrations) have decreased". The data in Table 4.1 accompanying this statement show a decrease of about 10% in predicted ethanol concentrations. I have two questions:

- a. What are the non-motor vehicle sources? It seems surprising that there are sufficient

stationery sources of ethanol that they would dominate those associated with motor vehicles.

Response: Ethanol is commonly used as a solvent, especially in consumer products. Everyday products from mouthwash to air fresheners, and many household-cleaning products contain ethanol. The 2003 baseline inventory for a non-ethanol fuel contains about 32 tons/day of ethanol, of which 24 tons/day comes from consumer products.

- b. What is the difference between the data cited in Table 4.1 of Appendix B and Table 4.6 of the report? The former cites concentrations of ethanol, for example, of 41-45 ppb while the latter cite 78-165 ppb for the maximum 1-hour average.

Response: The data in Table 4.1 of Appendix B represent model results for an August (summertime) ozone episode day. The data in Table 4.6 are estimated annual maximum or populated-weighted concentration values. The two tables may have widely different values, particularly for primary pollutants where the maximum value typically occurs under stagnant wintertime conditions.

On page B-43, it is stated that there are large discrepancies between predicted and observed 3-hour average concentrations for the Los Angeles site but that others are of the same order of magnitude. This might be strictly correct but the differences are still factors of two or more at some non-Los Angeles sites. Rewording of these sentences might be appropriate.

Response: There is insufficient discussion of the results presented in Table 6.4. Model results and measured data also differ significantly at other sites. For example, at Anaheim, the 1,3-butadiene 3-hour average concentration was measured at 0.3 ppb, while the model predicted an extremely lower concentration, measured formaldehyde is almost twice the predicted values, and measured acetaldehyde is about three times higher than what the model predicts. At Riverside, measured benzene is almost twice the predicted value at 0600, but at 1100 the measured benzene 3-hour-average concentration is three times the predicted value. The text on page B-43 is now revised.

Minor Comments:

1. In the fifth paragraph of the Executive Summary (starting “It is possible that ethanol’s propensity..”), it should be made clear that this discussion refers to the charcoal canister used for vapor control on automobiles.

Response: The suggested change has been incorporated into the report.

2. The ethanol concentration in fuel is sometimes given in % by weight and sometimes in % by volume. It would be very helpful to the reader to give it in both units throughout.

Response: The suggested change has been incorporated into the main report.

3. On page 32, line 6 of Section 4.2.3.3, the end of the sentence “The results are reported in....” is missing.

Response: The text has been corrected.

4. It is not clear to me what “Upper Baseline” and “Lower Baseline” mean in Table 4.6.

Response: Upper and lower baseline refer to baseline 1997 concentrations estimated under a variety of methods discussed in Section C-3 of Appendix C. The highest estimated 1997 concentration became the "Upper Baseline" and the lowest estimated 1997 concentration became the "Lower Baseline." The estimated future year concentrations were generally made starting with the upper and lower baselines and then applying model results to account for changes from the 1997 "baseline". The procedure for estimating future year concentrations is described in Section C-4 of Appendix C.

5. In Table 6.4, the predicted acetaldehyde concentrations are given to 4 significant figures in some cases; 2 significant figures is probably more appropriate.

Response: The model results in Table 6.4 have been revised to duplicate the number of significant figures of the measurements.

D-1.3. Dr. Donald Lucas of the University of California at Berkeley and Lawrence Berkeley National Laboratory

This letter contains my review of the California Air Resources Board document titled “Air Quality Impact of the Use of Ethanol in California Reformulated Gasoline.” This reviews covers the following parts of this document and several other documents, including the following:

1. Air Quality Impact of the Use of Ethanol in California Reformulated Gasoline – Staff Report (Nov. 18, 1999).
2. Appendix A - Emissions (Nov. 10, 1998).
3. Appendix D – Responses to Scientific Peer Review and Public Comments (Nov. 10, 1999).
4. Attachment A1 – Peer Review of Organic Gas Emission Profiles.
5. Other documents mentioned and/or cited in the above reports.

My review focused on the Executive Summary and Section 3 of the main document, Appendix A, and Sections D-1, D-2 and D-4 of Appendix D.

The purpose of the study was to analyze the environmental fate and transport of ethanol in air, surface water, and groundwater (Executive Order D – 5 – 99). The analysis estimates the changes in ambient air concentrations of potentially detrimental contaminants of the exhaust and evaporative emissions components and subsequent reaction products that would result from substituting ethanol-blended gasolines for gasoline blended with MTBE.

There were few conclusions drawn directly from the part of the work reviewed here. The emissions predicted were used in modeling to calculate how the atmosphere would change as a result of increased use of ethanol in gasoline. The atmospheric results themselves are only part of environmental impact.

The predicted changes in emissions expected from using ethanol in gasoline appear reasonable, both in the direction and magnitude of the changes. With no MTBE in the gasoline, MTBE

emissions should decrease to approximately zero (there may be a trace amount of MTBE in future fuels, but its concentration will be capped at 0.05% by the proposed CaRFG3 regulations). Compared with emissions expected for a 2003 fuel with MTBE, ethanol emissions will increase, with the value depending on the level of ethanol in the fuel. Ethanol containing fuels will have higher acetaldehyde emissions and could have lower levels of CO, depending on the amount of oxygenate used. Fuels without oxygen will produce more CO, but no ethanol or MTBE emissions. The predicted levels of NOx and reactive organic gases (ROG) are unchanged.

The calculations presented in this study appear to be consistent and reasonable, and are well documented. The calculations are complicated, and there are many assumptions made regarding emissions. These include the need to predict what fuel will be used in 2003, what the vehicle fleet will be, and what other emissions are significant. In this regard, it is difficult to determine exactly what the best set of assumptions should be, and how significant the results are from a statistical viewpoint. This is not to say that the results are incorrect, but that the uncertainties are large, and additional work needs to be done. The ARB recognized that the results rely on engineering judgement, and that the results need to be confirmed by the planned field measurements.

In developing the emission estimates for 1997 and 2003, the ARB made many adjustments to the profiles developed for MTBE-based CaRFG2. Changes were made for several compounds to be consistent with the fuel. Prof. Robert Harley of UC Berkeley reviewed the emission factors previously, and suggested several changes that were adopted by the ARB. I have no further suggestions. It is important to continue the early review process, as it allowed corrections to be made earlier in the process, probably saving considerable time and resources.

Response: The ARB staff agree.

Future gasoline compositions used in this study are predicted. Even though they may not be the exact formulations that will be sold in California in 2003, they are not unreasonable. The calculations in this study were performed as the new proposed Phase 3 Reformulated Gasoline (CaRFG3) regulations were being written, and both studies have similar deadlines. Since the CaRFG3 regulations may be adopted soon, the follow-up study suggested here should incorporate these changes. The timing of these two related studies made it difficult to use the information generated in the CaRFG3 regulation process, which was ongoing during the same period as this study. While better results could have been obtained by better coordinating the studies, time constraints placed on the ARB prevented this. While I do not think that the results from this study would change significantly if more time were allowed, care must be taken in balancing the need for a timely decision with the effort and time needed to produce sound scientific results.

Response: The ARB staff agree.

The effect of changing CO emissions when oxygenated fuels are used is accounted for in this study. Since CO acts as an organic compound in terms of ozone formation, it must be combined with other emissions. CO is treated here as other compounds, using the well-established and reviewed reactivity. The ARB is consistent in their approach. Whitten (1999) suggested a higher value for the reactivity of CO, and the ARB responded in detail. While the calculations presented by Whitten appear correct, it is difficult to justify using different models and scenarios for a single species. The value of examining issues such as these should not be underestimated, and the continued input from outside experts such as Whitten should be encouraged.

Response: The ARB staff agree.

The effect of consumer commingling, where ethanol-containing and ethanol-free gasolines are mixed, produces a fuel with a higher Reid Vapor Pressure (RVP). The mixed fuel would increase non-exhaust emissions. Under current federal law, where most of the gasoline in California is required to have an oxygenate, it is likely that commingling would not be a significant problem, since all gasolines would probably contain ethanol. However, Governor Davis has requested a waiver (April 12, 1999) from the EPA, and the ARB has supported this request. If granted, commingling could be more common. The effect of a waiver on commingling should be researched in a timely fashion, and potential solutions should be examined.

Response: The ARB staff agree.

The mileage penalty that occurs when using oxygenated fuels was not considered in this study. The mileage penalty is well known from previous research, and could be added as a simple factor. The small change will probably not effect these results, but they should be included in future work.

Response: Relative to typical current CaRFG2 made with MTBE, CaRFG2 containing 2 wt% oxygen as ethanol would only provide a slightly different fuel economy (change of 0.6% or less). CaRFG2 with 3.5 wt% oxygen would likely provide less fuel economy (by ~2%) than current gasoline, while a non-oxygenated CARFG2 would improve fuel economy by ~2%. However, mass emissions rate should not change in proportion to the change in fuel economy. The Predictive Model tends to force emissions to meet constant standards regardless of the oxygen content. The model is built from data on emissions versus oxygen content of gasoline. with emissions measured in mass per mile, not in mass per volume of fuel.

A small number of vehicles were tested at the ARB laboratory in El Monte. Three different commercially available fuels were used, including an ethanol-blend. However, the fuels are not representative of the fuels expected to be sold in 2003, and the ethanol-blended fuel had a very low sulfur level of approximately 1ppm (the sulfur level in the fuel is known to have a significant effect on exhaust emissions). The vehicles are not representative of the fleet either in terms of vehicle number, miles driven, or fraction of emissions. Given the high cost and difficulty of this type of vehicle testing, this is a disappointing part of the study. It is not clear how the criteria for vehicle selection were made. Half of the vehicles were required to have mid-range emissions of hydrocarbons. The average model year was 1981, and only one car was Japanese. While it is important to learn how the mid- and high-emitters will perform on any new fuels, the ARB has previously reported that it is nearly impossible to test these types of cars under current testing protocols because of their non-reproducible behavior.

Response: We planned to test vehicles that contribute the most to emissions. This is not the same group of vehicles that have the highest vehicle miles traveled (VMT). While the average emission rates and test variability were higher than desired, the results are not a crucial part of our conclusions.

Running and evaporative losses were not measured directly. The composition of emissions expected was estimated in part by measuring vapor in equilibrium with the liquid fuel. Since these emissions are becoming a larger fraction of the total vehicle emissions, it is important to know these emissions, especially since material permeability and cannister performance is not well understood for fuels with varying ethanol levels. The ARB has noted the limitations of their testing in this

study. Their conclusions are qualitative, and they claim that they do not contradict the model profiles. Given the uncertainties the claim is probably true, but of little value.

Response: The lack of evaporative emission measurements taken on commercial fuels did not directly bear on evaluating the profiles used to represent evaporative emissions in the photochemical modeling. Like the data taken in the commercial fuel study, the modeling input profiles are gasoline composition profiles and their corresponding headspace compositions, rather than actual hot-soak and diurnal/running compositions. While the substitution of gasoline and headspace compositions for actual evaporative emissions introduces error, that error could not have been estimated by comparison to speciated evaporative emissions from the commercial fuels. As noted by the reviewer, those fuels cannot be viewed as typical of future MTBE-free CaRFGs.

With regard to evaluating the accuracy of the headspace profiles (that is, their relationship to the gasolines), we note in the report that they have been calculated with an equilibrium model that has been validated previously. Thus, we do not view the discrepancies in Table 6.1 with the measured fuel/headspace ratios (which in part reflect experimental error) as sufficient to discredit the equilibrium model.

In summary, the ARB has produced a set of emissions expected in the 2003 if ethanol replaced MTBE in California gasolines. The results are a good starting point for evaluating the environmental impact of ethanol in fuels, and provide the necessary data for further analysis. This type of modeling effort should continue, especially as the composition of the new fuels becomes more certain.

Response: The ARB staff agree.

D-1.4. Professor John Seinfeld of the California Institute of Technology

I am reporting to you on Appendix B Photochemical Modeling. (I looked at the other reports but did not read them closely.) I have reviewed the model application protocol reported in Appendix B and find it to be not inconsistent with standard practice in South Coast Air Basin photochemical modeling. Replacement of the CBM with SAPRC-97 was an important feature. The use of the model simulations in a relative sense enhances their value in looking for differences between scenarios. I have not reviewed the emissions profiles for the MTBE and ETOH cases; I assume they accurately reflect those profiles. The predicted direction of differences in O₃ and other pollutants between the scenarios can be considered to be accurate. It is noteworthy that the predicted differences in O₃ between the MTBE and ETOH cases are small. (Interestingly, this was also the case a number of years ago when comparisons between gasoline and reformulated gasoline were being made.) Assuming that the MTBE and ETOH emissions profiles and amounts are accurate, this says that other factors are governing the overall concentration of O₃, not these ingredients. One can gauge if this makes sense from the change in magnitude of emissions of gaseous products associated with MTBE and ETOH. Presumably this is the case.

Response: The ARB staff agree.

In summary, the photochemical modeling is consistent with current practice. There are no evident danger signals associated with the results. Model performance in an absolute sense could be better, but the use of simulations in a relative sense should bypass these difficulties.

As you have requested, I have read Section D-3 of the report. Gary Whitten's analysis of the effect of CO on ozone formation, as simulated in a three-dimensional model, is correct. The question, though, is not whether Whitten is correct, but what scale is being used to judge reactivity. The ARB has utilized Carter's MIR scale, which is not based on three-dimensional, multiday simulations. Most would agree that three-dimensional, multiday simulations are preferable to trajectory box simulations in assessing reactivity. This point was made by the ARB's Reactivity Advisory Committee at its last meeting. Moreover, the fact that peak ozone reactivities differ between the MIR scale and those predicted on the basis of a 3D model points not to a weakness of 3D models, but to a weakness of the trajectory model MIR simulation. That having been said, however, it is recognized that the ARB has invested in the Carter MIR scale for judging reactivity and changing lock stock and barrel over to a 3D airshed model scale is a nontrivial undertaking. The question is whether the reactivity of CO should be increased by 1.65 in the current application. The ARB response argues that in the interests of consistency they do not wish to alter the scale that has been used and that population exposure correlates better with that predicted by the MIR scale than peak ozone anyway. Short of basing all reactivities on 3D model simulations, I cannot recommend that the ARB make this one single adjustment.

Response: The ARB staff agree.

D-2. References

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